The Less Refrangible Spectrum of Cyanogen, and its Occurrence in the Carbon Arc.

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[Plate 7.]

Introductory.

In connection with Prof. Strutt's investigations of the interaction between the active modification of nitrogen and certain compounds of carbon,* it became necessary to compare the resulting spectra with the spectrum given by cyanogen under the more usual conditions of experiment. It was then discovered that while precise measurements of the well known bands in the violet and ultra-violet had been made by Kayser and Runge, only roughly approximate positions had been tabulated for the bands, degraded in the opposite direction, which appear in the less refrangible parts of the spectrum. In view of the interest of these bands, arising from their possible occurrence in association with the violet bands in certain celestial bodies, as well as from the regularity of their structure, a new series of measurements has been undertaken.

The spectrograph chiefly employed for the determination of positions was one of the Littrow type, giving a linear dispersion of 57 tenth-metres per millimetre at 6700, and 16·5 tenth-metres per millimetre at 4700, the length of spectrum between these points being 6·7 cm. A quartz spectrograph giving 2 cm. for the same range of spectrum was also utilised for ready comparison of the spectra obtained from different sources.

Sources of the Spectrum.

The spectrum has been obtained from different sources, as follows:—

Flame.—The cyanogen was prepared by heating mercuric cyanide, and after drying by passage through a tube containing phosphorus pentoxide it was burned at a glass nozzle. In some of the observations the flame was surrounded by a glass chimney into which a stream of oxygen was passed, and under these conditions the intensity of the spectrum was greatly increased.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 228.

Vacuum Tube.—On account of the rapid decomposition of the gas by the electric discharge, a constant stream was passed through the vacuum tube during the exposure of the plates, which amounted in some cases to more than three hours. An "end-on" tube was of necessity employed, because of the dark deposit of paracyanogen which is quickly formed on the walls of the tube in the path of the discharge. It was further necessary to remove and clean the glass or quartz plate through which the light was transmitted to the spectrograph, about once in 20 minutes.

As obtained in this way the bands were very brilliant, and with careful adjustment of the supply of gas the spectrum was more easily maintained than in the case of the flame.

Active Nitrogen.—Prof. Strutt has shown that when certain compounds of carbon such as acetylene and carbon tetrachloride are brought in contact with "active nitrogen," the resulting luminous glow or flame gives a brilliant spectrum of cyanogen. In the case of acetylene, the flame is of a lilac tint, like that of the burning gas, but with carbon tetrachloride the luminosity is orange in colour and the red spectrum of cyanogen is more strongly developed in relation to the violet. The cyanogen spectrum produced in this way from carbon tetrachloride offers special advantages for investigations of the regularity of the bands, in consequence of the better development of the more refrangible bands of the series, which are very feeble in the spectra obtained from the other sources. The violet cyanogen bands in this spectrum are considerably different in detail as compared with those given by the cyanogen flame or carbon arc.* For convenience of reference the cyanogen spectrum obtained by the aid of active nitrogen may be called the "glow-cyanogen" spectrum.

Description of the Spectrum.

The main features of the red cyanogen spectrum, as seen with instruments of small dispersion, are well known. The spectrum consists of a succession of bands—degraded towards the red—which are especially intense in the less refrangible parts of the visible spectrum, and become generally weaker as the blue is approached (Plate 7, figs. 1 and 2). With adequate resolving power each band is seen to be composed of three flutings, the heads of which form a triplet with the narrower pair towards the red. On the more refrangible side of most of the triplets there is an additional faint head, separated from the first component by an interval slightly greater than that between the two closer members of the triplet. The triplets, however, are the most striking features of the spectrum when moderate dispersion is employed.

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* See Strutt and Fowler, 'Roy. Soc. Proc.,' this vol., p. 105.

The spectrum shows considerable variations according to the source from which it is obtained. As will be seen from the data given in Table I, the relative intensities of some of the bands are far from being identical in the different spectra. The band near D (5859) is a notable example, being strong in the vacuum tube and glow-cyanogen spectra, but weak in the flame. Also, the bands more refrangible than 5240 only occur as traces in the flame, but are shown with moderate intensity in the vacuum tube, and better still in the glow-cyanogen. A complete comparison of the spectra from the three sources, however, was complicated by the presence of bands belonging to other spectra in the case of the flame and vacuum tube. In both flame and vacuum tube the bands of the Swan spectrum of carbon appeared, and the hydrocarbon band 4315 was also usually present. The vacuum tube spectrum generally showed, in addition, the carbonic oxide bands 6079, 5610·26, 5198·33, and 4835·44, probably on account of the imperfect removal of water vapour. The vacuum-tube spectrum further differed from the flame spectrum in showing some of the nitrogen flutings, though as a result of the constant changing of the cyanogen in the tube the bands of the first positive group were only shown as feeble traces, and those of the second positive group were not strong enough to be troublesome in the region under investigation.

In accordance with many previous observations,* it was found that when the cyanogen flame was fed with oxygen the whole spectrum was greatly increased in brightness, and that the Swan bands were especially intensified (fig. 4, *a*). The relative intensities of the various cyanogen bands, however, were not greatly affected.

The spectrum produced by carbon tetrachloride in active nitrogen was practically free from contamination with other spectra. There were practically no indications of the hydrocarbon band 4315 or of the bands of the Swan or carbonic oxide spectra. Bands of nitrogen were present, but they were not strong enough to interfere with the identification of the cyanogen triplets.

It should be remarked further that the visibility of the fainter triplets varied greatly with the source and with the dispersion of the instrument employed. In some cases these faint bands were masked by the structure lines emanating from adjacent stronger heads.

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* *E.g.*, Morren, 'Ann. de Chim. et de Phys.,' 1865, series 4, vol. 4, p. 312.

Determination of Wave-Lengths.

The bands in the extreme red were observed visually, and the positions of those less refrangible than 7000 were determined by the use of a wave-length spectroscope.

For the part of the spectrum more refrangible than 7000 the wave-lengths were determined from photographs taken with the Littrow spectrograph, the iron arc being used as a term of comparison. Sufficient iron lines were included in the measures to indicate the corrections to be applied to the wave-lengths calculated by the use of the Cornu-Hartmann formula.

It should be explained that the wave-lengths tabulated can only be regarded as close approximations. As in the case of flutings in general, there is evidence that the heads are complex groups of lines, and the measured wave-lengths will, therefore, depend to some extent upon the dispersion and resolving power of the instrument employed. In order to obtain a consistent system of wave-lengths for discussion of the regularity of the bands, the values tabulated, with the exception of those for the bands in the extreme red, were obtained from a single photograph of the spectrum of "glow-cyanogen," in which the dispersion at D was 38 tenth-metres per millimetre, and the purity of the spectrum at the same place 4000 (fig. 1). Spectra of greater purity were also obtained, but the identification of the heads was in some cases less certain on account of the interference of structure lines belonging to adjacent flutings.

An attempt has been made to include all the fainter bands so as to make the investigation of the structure of the spectrum as complete as possible. Some of the heads would not have been identified as such if their existence had not been indicated by the arrangement of the bands in series.

The positions of the various bands are indicated in Table I. Column 1 gives the wave-lengths, Columns 2, 3, and 4 the relative intensities in the flame, vacuum-tube, and glow-cyanogen spectra respectively, as roughly estimated on a scale of 10 for the brightest band; Column 5 shows the oscillation frequencies *in vacuo*; Column 6 indicates the series to which each band belongs according to the analysis which is given later, and Column 7 the difference (in frequency) between the value observed and that calculated from the series equation.

Table I.

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
7435				13446	76	63	+4	Most refrangible head of a band observed visually.
7283				13727				Visual observations.
7273				13746				
7259				13772	77	64	0	
7119				14043				Visual observations.
7110				14061				
7091				14098	78	65	−4	
6961·6		1	1	14361	74	60	−2	Probable most refrangible head of a faint triplet.
6954·9				14374				
6946·0	2	2	1	14393				
6928·2				14430	79	66	−3	
6818·2				14663				Also a faint head at 6780·2 (14745).
6809·8	<1	2	3	14681				
6793·1				14717	75	61	−2	
6657·2				15017				Also a faint head at 6621·4 (15098).
6648·7	4	9	7	15036				
6632·2				15074	76	62	−1	
6503·0				15373				Also a faint head at 6467·3 (15458).
6494·7	9	10	10	15393				
6479·3				15430	77	63	−1	
6457·0				15483				
6448·9		1	1	15502				
6433·3				15540	73	58	+2	
6355·5				15730				
6347·9	10	9	6	15749				
6332·8				15786	78	64	−1	
6301·8				15864				Also a faint head at 6272·5 (15938).
6294·3		1	2	15883				
6280·0				15919	74	59	0	
6214·4				16087				
6206·7	6	4	1	16107				
6192·3				16145	79	65	+2	
6154·1				16245				Also a faint head at 6124·4 (16324).
6147·4	<1	3	3	16263				
6133·6				16299	75	60	−1	
6013·5				16625				Also a faint head at 5984·9 (16704).
6006·9	2	6	6	16643				
5993·5				16680	76	61	−2	

Table I—*continued.*

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
5866·2		<1	<1	17041	73	57	0	Probable most refrangible head of a faint triplet; other components masked by next band.
5878·3	2	9	9	17007				Also a faint head at 5850·6 (17078).
5872·2				17025				
5858·7				17064	77	62	0	
5749·3	5	7	7	17389				Also a faint head at 5722·4 (17470).
5743·3				17407				
5730·8				17445	78	63	−1	
5747·9		1	1	17393				Superposed on previous stronger triplet, and not separately observed with small dispersion.
5742·2				17410				
5729·1				17450	74	58	−1	
5625·6		2	2	17771				Overlapped by next band. Both are involved in the 5635 band of the Swan spectrum in the flame and vacuum tube.
5619·4				17791				
5607·3				17828	79	64	0	
5616·3	3	3	4	17800				Also a faint head at 5591·2 (17880).
5611·1				17817				
5598·9				17856	75	59	0	
5490·8	2	5	5	18207				Also a faint head at 5467·4 (18285).
5485·5				18225				
5474·1				18263	76	60	−1	
5370·9	2	4	6	18614				Also a faint head at 5348·4 (18692).
5365·6				18632				
5354·8				18670	77	61	−2	
5255·4	2	3	5	19023				Also a faint head at 5233·2 (19104).
5250·7				19040				
5240·2				19078	78	62	−1	
5171·6			1	19331				Also a faint head at 5150·4 (19411).
5167·5				19346				
5156·3				19388	75	58	+2	These are superposed on the 5165 band of the Swan spectrum in the flame and vacuum tube.
5144·9			1	19431				
5139·6				19451				
5130·3				19487	79	63	0	
5058·2		1	1	19765				
5054·2				19780				
5043·7				19821	76	59	+1	
4949·7	1	2	3	20198				Also a faint head at 4931·3 (20273).
4945·9				20213				
4936·4				20252	77	60	0	

Table I—*continued.*

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
4845·9				20630				Also a faint head at 4828·3 (20706).
4842·3	1	?	4	20646				
4833·2				20685	78	61	−1	
4798·1				20836				
4794·6			1	20851				
4785·5				20891	75	57	+1	
4746·0				21065				
4742·3			2	21081				
4733·3				21121	79	62	+1	These are superposed on the 4737 band of the Swan spectrum in flame and vacuum tube.
4694·6				21295				
4691·3			2	21310				
4682·6				21350	76	58	0	

In addition to the bands given in Table I, there were indications of fainter bands, the wave-lengths of which could not be satisfactorily determined from the photographs available. The arrangement of the bands in series, however, permits the calculation of the positions of these faint bands, and for completeness, the calculated wave-lengths of the more refrangible heads are stated below.

Fainter Cyanogen Bands.

Wave-length (air).	Frequency (*in vacuo*).	Series.	
		p.	*m.*
5398·4	18519	73	56
5274·8	18953	74	57
5005·6	19972	73	55
4893·2	20431	74	55
4584·0	21809	77	59
4489·5	22268	78	60
4398·8	22727	79	61
4283·3	23340	77	58

Series Relationships.

The triplets comprising the spectrum appear to be essentially similar to each other, and equally spaced, or nearly so, when estimated on the scale of oscillation frequencies. In the discussion of the distribution of the bands it will therefore suffice to consider the more refrangible members of the triplets.

An analysis of the frequencies has shown that the bands can be arranged in series which are similar to those in which the first positive bands of nitrogen have been arranged by Cuthbertson* and Deslandres.† This is shown in Table II, from which it will be seen that the bands form series of the usual type, whether taken in vertical or horizontal order. The bands in any single series are closely represented by Deslandres' formula, $n = A + Bm^2$, in which A and B are constants, and m is a number increasing by unity for successive values of n.

If we consider, say, the vertical series, it is clear that the equation calculated from one of them should be applicable to the remainder by a mere change in the value of A, and the figures show that A will vary in such a manner for the different series that it can be represented by another equation of the same form. Hence, all the bands may be included in Deslandres' general equation

$$n = A + Bm^2 - Cp^2.$$

Table II.—Regularity of Cyanogen Bands (oscillation frequencies *in vacuo*).

p …	79		78		77		76		75		74		73
m.													
66	14430												
	1715												
65	16145	2047	14098										
	1683		1688										
64	17828	2042	15786	2014	13772								
	1659		1659		1658								
63	19487	2042	17445	2015	15430	1984	13446						
	1634		1633		1634		1628						
62	21121	2043	19078	2014	17064	1990	15074						
			1607		1606		1606						
61			20685	2015	18670	1990	16680	1963	14717				
					1582		1583		1582				
60					20252	1989	18263	1964	16299	1938	14361		
							1558		1557		1558		
59							19821	1965	17856	1937	15919		
							1529		1532		1531		
58							21350	1962	19388	1938	17450	1910	15540
									1503				
57									20891				

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* 'Phil. Mag.,' 1902, [6], vol. 3, p. 348.

† 'Compt. Rend.,' 1902, vol. 134, p. 747.

The coefficients B and C, which are equal to half the second differences in the vertical and horizontal columns respectively, appear to have the same value in the case of cyanogen, and the general equation may therefore be written in the simplified form

$$n = \mathrm{A} - \mathrm{B}(p^2 - m^2).$$

By the use of this equation, a greater range of values of m may be utilised than in calculations based on a single series, and a more accurate representation of the several series may be expected on account of reduced extrapolation. In the actual calculation all the bands have been used in the determination of the constants, and the resulting equation may be written

$$n = 12{\cdot}90\,[(p+0{\cdot}6)^2 - (m+0{\cdot}8)^2] - 9741.$$

For the bands tabulated, p ranges from 73 to 79, and m from 56 to 66, and, as will be seen from the values O − C (observed *minus* computed) given in Table I, the equation represents all the bands very closely, and probably within the limits of error.

Occurrence in the Carbon Arc.

The occurrence of the violet and ultra-violet cyanogen bands (4606·33, 4216·12, 3883·55, 3590·48) in the spectrum of the arc between carbon poles at once suggests that the less refrangible bands under consideration should also appear in company with them. Hitherto, however, their presence does not seem to have been recognised.

Besides the violet and ultra-violet bands of cyanogen, and the Swan bands of carbon (5635·43, 5165·30, 4737·18, 4381·93), the carbon arc shows an immense number of fine lines in the yellow and red, which, so far as we are aware, have not previously been assigned to any definite substance. These lines evidently belong to a banded spectrum, although no distinct heads of flutings are recognisable with the instruments of high dispersion which are most frequently employed for so bright a source (see Plate 7, fig. 5). In observations with small dispersion, however, the lines are seen to be much more densely crowded together in certain places, giving the appearance of ill-defined bands, and comparison photographs, such as those in Plate 7, fig. 4, indicate that these brighter places in the arc spectrum coincide in position with the heads of cyanogen bands. All the chief cyanogen bands from the extreme red to that at 5240 can easily be traced in the arc spectrum in this way.

Conclusive evidence of a close relation between the two spectra is furnished by comparisons obtained with the Littrow spectrograph to which reference has been made. The resolving power of this instrument is sufficient to show a great number of the lines composing the cyanogen bands, while the dispersion is not too great to obscure the corresponding maxima in the spectrum of the arc. The photographs (Plate 7, fig. 2) show very clearly that not only are the brightest places in the arc spectrum coincident with the heads of the cyanogen bands, but that the structure lines are, for the most part, the same in both cases. From the red, as far as the Swan band 5635, the coincidences are very numerous, and some of the separate heads in the cyanogen flutings can be traced in the arc when the cyanogen spectrum is made use of as a guide; the three heads of the band 6333 are especially distinct in the arc spectrum. The comparison clearly indicates that the highly complex spectrum of the carbon arc in the red and yellow is, in the main, due to cyanogen.

The correspondence between the two spectra, however, is not complete when the cyanogen spectrum is obtained from a vacuum tube. While the vacuum-tube spectrum shows comparatively clear spaces between sharply defined bands, the arc spectrum exhibits an unbroken succession of lines with only ill-defined maxima to mark the positions of the heads of the bands. It would thus appear that the condition of the glowing gas in the arc is not identical with that of the gas in the vacuum tube. Other comparisons have shown, however, that a closer resemblance to the arc spectrum is given by the flame of cyanogen, either when the gas is burning in ordinary air or fed with oxygen. In this case the bands are less clearly separated than in the vacuum-tube spectrum, and the heads are less distinctly marked, when the dispersion is sufficient to resolve the bands into their component lines (Plate 7, fig. 3). Further, the arc bands, as a whole, are more like those of the flame spectrum in intensities than those of the vacuum tube, the variation of the band near D being especially noticeable. It is probable that the greater similarity between arc and flame than between arc and vacuum tube is to be attributed to the nearer equality of pressure conditions, as some band spectra are known to vary with pressure.*

Experiments on the changes in the spectrum when the arc is surrounded by different gases have yielded additional interesting evidence as to the cyanogen origin of the less refrangible part of the arc spectrum. The arc was enclosed in a glass globe, provided with arrangements for exhaustion, and for the admission of any desired gas.† When the globe was merely evacuated, hydrogen was liberated as the poles became heated, and the arc was then passing in rather impure hydrogen at a pressure of a few millimetres. Under these conditions, the violet bands of cyanogen were much

* Deslandres, 'Compt. Rend.,' 1904, vol. 139, p. 1174.

† See 'Phil. Trans.,' 1909, A, vol. 209, p. 449.

reduced in intensity, and the many-lined spectrum in the yellow and red practically disappeared (fig. 6, *d*), as would be expected on the supposition that this spectrum is due to cyanogen. Hydrogen was itself represented by H_α, etc., and numerous lines of the secondary spectrum, and the hydrocarbon band 4315, which is not seen in the arc in air, was also present. The Swan band 6188 was also at times well developed in the spectrum, presumably because it was rendered more visible by the removal of the cyanogen band lines, on which it is superposed when the arc is observed in air. It would thus appear that the nearly total removal of nitrogen from the vicinity of the carbon poles results in the disappearance of the great majority of the lines in the yellow and red, and thus supports the view that this part of the spectrum of the carbon arc in air is mainly due to cyanogen.

When the arc was passed in oxygen, either at atmospheric or at reduced pressure, the lines in question again disappeared, or nearly so, and the violet bands of cyanogen were weakened as in the previous experiment (fig. 6, *b*). At the same time, the Swan bands in the green were brightened, the orange band 6188 was easily photographed, and another band of the Swan spectrum less refrangible than H_α was occasionally observed. Both the orange band and the less refrangible one doubtless contribute to the spectrum of the carbon arc in air, but even the group beginning at 6188 can only be traced with difficulty. Bands of carbonic oxide, 5610, 5197, etc., were also occasionally seen when the arc was passed in oxygen, and in some of the observations of the arc *in vacuo*.

A similar experiment with chlorine surrounding the arc also indicated that the band lines under consideration were not produced in the absence of nitrogen.

There is accordingly abundant evidence to show that the great majority of the multitude of lines observed in the less refrangible part of the spectrum of the carbon arc in air are due to cyanogen, while a few of them represent the Swan spectrum of carbon. Bands of carbon and cyanogen thus account completely for the arc spectrum as observed under ordinary conditions.

Comparison with Celestial Spectra.

Among celestial bodies the violet bands of cyanogen have been observed in the spectra of the sun, stars of Secchi's fourth type, and comets. The laboratory experiments have given no evidence that the violet bands can exist apart from the red bands, except to an extent that can be accounted for by the greater intensity of the violet groups. Hence, when the violet bands appear with sufficient intensity in any source, the less refrangible bands may also be expected.

The presence of the ultra-violet band of cyanogen 3883 in the solar spectrum was first shown by Lockyer,* and the tables of Rowland indicate that the bands 4216 and 3590 are also represented among the Fraunhofer lines. All the bands, however, are feeble in the sun, and although the appearance of the less refrangible groups was scarcely to be expected, it nevertheless seemed desirable to make the comparison. Wave-lengths of the necessary degree of accuracy were obtained from photographs of the carbon arc taken with the ten-feet concave grating (fig. 5). Although the heads of the cyanogen flutings cannot be recognised in such photographs, accurate wave-lengths of the lines composing them can be obtained. Portions of the arc spectrum in the neighbourhood of the chief cyanogen bands were measured in detail and compared with the solar lines tabulated by Rowland, but no systematic coincidences could be established. The cyanogen spectrum thus appears to be too feebly developed in the sun to give appreciable indications of the less refrangible system of bands.

A photographic investigation of the Type IV stars made by Hale, Ellerman, and Parkhurst† has demonstrated the presence in the spectra of these stars of the violet bands of cyanogen, in addition to the Swan bands of carbon which were previously identified by Secchi in the visible spectrum. A number of narrow bands in the red and yellow, previously noted by Dunér and Vogel, were also shown in a photograph of the spectrum of 152 Schjellerup, but no significant coincidences with the less refrangible group of cyanogen can be certainly established. As in the solar spectrum. the violet bands do not appear to be sufficiently developed in this star to give much expectation of the visible manifestation of the red and yellow bands. Further comparison should be made when details of the red part of the spectrum become available for those stars of the fourth type in which the violet bands are more strongly developed.

As regards comets, bands in the red have occasionally been noted, but no accurate data are available.

Summary.

1. Revised wave-lengths are given for the bands forming the less refrangible part of the cyanogen spectrum. Numerous bands which have not previously been recorded are included.

2. The heads of the bands can be arranged in regular series similar to those constituting the first positive band spectrum of nitrogen.

3. There are considerable variations in the relative intensities of the

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* 'Roy. Soc. Proc.,' 1878, vol. 27, p. 308.

† 'Pub. Yerkes Observatory,' 1904, vol. 2.

various bands, according as the spectrum is obtained from the flame of the burning gas, from a vacuum tube, or from the luminous glow produced by the interaction of certain compounds of carbon with active nitrogen.

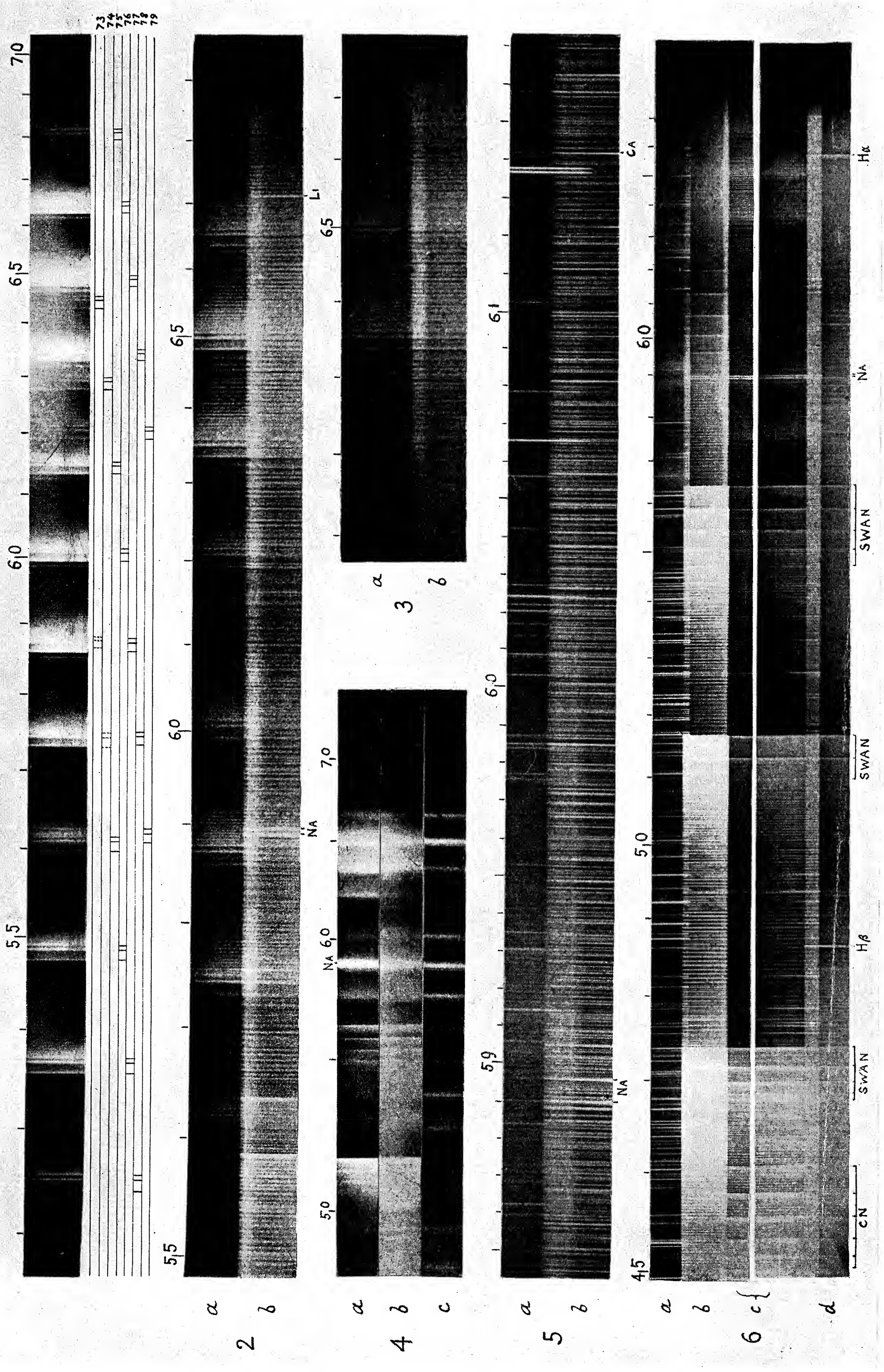
4. The complex spectrum of the carbon arc in the red and yellow is almost entirely due to cyanogen.

5. The spectrum of cyanogen in the sun is not of sufficient intensity to give visible indications of the red and yellow bands. Adequate data for comets and Fourth Type stars are not available for comparison.

DESCRIPTION OF PLATE.

1. Cyanogen spectrum produced by carbon tetrachloride in active nitrogen.
2. (*a*) Vacuum-tube spectrum of cyanogen.
   (*b*) Carbon arc comparison.
3. (*a*) Portion of flame spectrum of cyanogen.
   (*b*) Carbon arc comparison.
4. Small dispersion photographs—
   (*a*) Cyanogen flame fed with oxygen.
   (*b*) Carbon arc.
   (*c*) Cyanogen produced by CCl_4 in active nitrogen.
5. (*a*) Iron comparison spectrum.
   (*b*) Carbon arc (with 10 feet concave grating, 1st order).
6. (*a*) Iron comparison spectrum.
   (*b*) Carbon arc in oxygen at 10 in. pressure.
   (*c*) Carbon arc in air.
   (*d*) Carbon arc *in vacuo* (*i.e.*, hydrogen, etc.).

SPECTRA OF CYANOGEN AND CARBON ARC.



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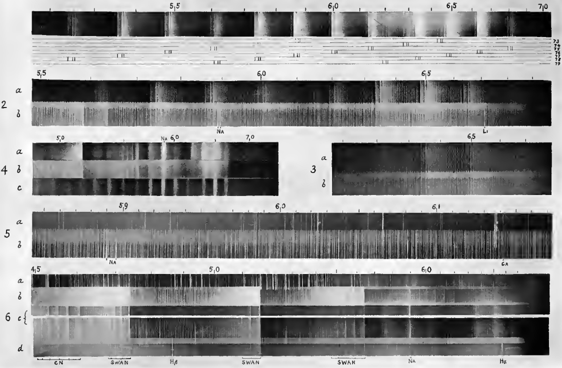

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